

## PATENT ABSTRACTS OF JAPAN

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(54) TREATING METHOD FOR SURFACE OF SYNTHETIC RESIN FILM

(57)Abstract:

PURPOSE: To provide method whereby the adhesive properties, etc., of a synthetic resin film are improved by mechanically rubbing the surface of the film with a specific surface treatment agent soln. and drying the surface.

CONSTITUTION: The surface of a synthetic resin film is mechanically rubbed with a soln. for a surface treatment reactive with the components of the surface and the dried. Examples of the film are polyester, polyamide, and polyamide films. In treating a polyimide film, a surface treatment agent based on an acrylsilane, an aminosilane, or an epoxysilane is used as the surface treatment agent reactive with the components of the surface of the polyimide film.

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DETAILED DESCRIPTION

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## [Detailed Description of the Invention]

[0001]

[Industrial Application] this invention relates to the surface treatment method of a synthetic-resin film of it having been [ for /, such as the adhesive property of a film, / improvement ] simple, and having excelled, in more detail about the surface treatment method of a synthetic-resin film.

[0002]

[Description of the Prior Art] A synthetic-resin film is used in many cases as the charge of plywood made to rival organic materials, such as inorganic material, such as a metallic foil, and other synthetic resin, through adhesives, an adhesion sheet, etc., for example, an insulating material, lead-wire covering material, etc. of a printed wired board. Such material is widely used for the electrical machinery and apparatus etc. By the way, when a synthetic-resin film uses it, compounding with other inorganic material and an organic material, it is required from viewpoints, such as electric and mechanical reliability, that an adhesive property with these other materials should be high. Therefore, surface treatment may be used for a synthetic-resin film for an adhesive improvement, giving it.

[0003] Before, the sandblasting method, the wet cleaning method, the corona-treatment method, the plasma treatment method, the dry type approach, etc. are enforced as the surface treatment method for an adhesive improvement of a synthetic-resin film. If surface treatment of a synthetic-resin film is performed by these methods, also in which method, a high adhesive property can be given compared with the case of being unsettled.

## [Problem(s) to be Solved by the Invention]

[0004] However, these conventional arts have a fault with expensive or cost and difficult stable processing. Moreover, in case a resin film is used as a charge of plywood made to rival other materials, to have an adhesive property with a still more expensive resin film is also desired from a viewpoint of the reliability of the charge of plywood.

[0005] Moreover, when using adhesives in the fully stiffened state, i.e., the state where the function as adhesives was demonstrated enough, the above-mentioned conventional art can also give a high adhesive property to a synthetic-resin film, and the improvement effect which was excellent compared with the unsettled film is shown. However, by the conventional surface treatment method, when adhesives use it in the state of un-hardening or semi-hardening, even if it is a processing film and is an unsettled film, there is no big difference to the adhesive property, and it has the fault that the adhesive improvement effect is not shown. Depending on the use, this fault may cause a serious defect and the improvement is desired.

[0006] for example, a resin film and the adhesives sheet of a semi-hardening state -- a hot calender roll - laminating -- a layered product -- forming -- the layered product -- metal mold -- even if it gives the conventional art to a resin film, the intensity of the interface of a resin film and adhesives is weak, when carrying out punching processing by punching, in case it carries out punching processing, it lacks an adhesives layer, falls and has a defect and a bird clapper Therefore, even if adhesives are in which state of the state where it does not harden, a semi-hardening state, and a hardening state, a surface treatment

method of the synthetic-resin film which can give a good adhesive property to a resin film is desired. [0007] Then, this invention persons solved the above-mentioned problem, could do stable processing in the low cost, have improved the adhesive property of a resin film, and even if adhesives were in which state of the state where it does not harden, a semi-hardening state, and a hardening state, as a result of repeating research wholeheartedly for the purpose of offering the surface treatment method of the synthetic-resin film which can give a good adhesive property, they resulted in this invention.

[0008]

[Means for Solving the Problem] The place made into the summary of the surface treatment method of the synthetic-resin film concerning this invention is to carry out rubbing of the front face of a synthetic-resin film mechanically, and dry it with a film surface component and the solution of coupling agent which can react.

[0009]

[Function] Rubbing of the front face of a synthetic-resin film is mechanically carried out with a film surface component and the solution of coupling agent which can react, and the surface treatment method of the synthetic-resin film concerning this invention can dry it, can remove the brittle layer currently formed on the surface of the film, and can perform chemical modification on a front face simultaneously. A stabilizer, an additive, a low-molecular-weight resinous principle, etc. carry out bleeding of the front face of a synthetic-resin film preferentially at the time of film formation, consequently a surface brittle layer is formed, and existence of this layer is considered to cause an adhesive fall. Therefore, this surface brittle layer is removable by carrying out rubbing of the film front face to a film surface component mechanically with the solution of coupling agent which can react, namely, applying physical mechanical power to a film front face under the existence of the solution of coupling agent. Furthermore, while removing a surface brittle layer, chemical modification is performed on a film front face, and the outstanding adhesive property can be given. In the case of the polyimide film especially manufactured with the solution cast, bleeding happens remarkably by existence of a solvent, formation of a surface brittle layer is also said to be remarkable, and it is supposed that formation of this surface brittle layer is the low adhesive property of a polyimide film the cause. Therefore, the surface treatment method concerning this invention is used suitable for a polyimide film, and can give a good adhesive property to a polyimide film.

[0010]

[Example] Hereafter, the surface treatment method of the synthetic-resin film concerning this invention is explained in detail based on a drawing.

[0011] The surface treatment method of the synthetic-resin film concerning this invention can carry out rubbing of the front face of a synthetic-resin film to a film surface component mechanically with the solution of coupling agent which can react, can dry the solvent of the coupling-agent solution which adhered on the film, and, thereby, can perform simultaneously removal of a surface brittle layer, and surface chemical modification. It means applying physical mechanical power under the existence [ carry out / rubbing of the front face of a synthetic-resin film / mechanically / in this invention / with the solution of coupling agent ] of the solution of coupling agent by the front face of a synthetic-resin film. The method of specifically wiping or grinding the front face of a synthetic-resin film against base materials, such as a nonwoven fabric into which the solution of coupling agent was infiltrated, is mentioned. In this process, since the solution of coupling agent adheres to the front face of a synthetic-resin film, the process which dries this solution is needed. The technology of many well-known as the dryness method can be applied, and which methods, such as an air drying, a forced drying, and stoving, may be used.

[0012] For example, the processor 10 shown in drawing 1 is equipped with the roll 12 for rubbing and drying furnace 14 which were produced by base materials, such as a nonwoven fabric, the roll 12 for rubbing is flooded with the solution 13 of coupling agent, and the solution 13 is infiltrated into it. And the synthetic-resin film 16 lets out from the film delivery roll 18, and is conveyed with the roll 20 for conveyance to the roll 12 for rubbing, and a drying furnace 14, and it is constituted so that a tension cut may be carried out by the nip roll 22 and it may be rolled round by the film winding roll 24. Therefore,

rubbing of the front face of a film 16 can be mechanically carried out with the solution 13 of coupling agent by conveying a film 16 by constant speed in this equipment 10, and rotating the roll 12 for rubbing. Although the same direction as the feed direction of a film 16 is sufficient as the hand of cut of the roll 12 for rubbing, its opposite direction is effective. After that, a film 16 is dried with a drying furnace 14, and surface treatment is carried out.

[0013] Here, although the film of many well-known as a synthetic-resin film said to this invention is applied and it is not limited especially, polyester film, a polyamide film, and a polyimide film are applied preferably, and a polyimide film is applied still more preferably. The stabilizer, the additive, the low-molecular-weight resinous principle, etc. would carry out bleeding of the front face of these synthetic-resin films preferentially at the time of film formation, consequently a brittle layer will be formed in a film front face, and existence of this layer has caused the adhesive fall. Since especially a polyimide film is manufactured with the solution cast, bleeding happens remarkably by existence of a solvent, and formation of a surface brittle layer is also considered to be remarkable, and is used suitable for the art of this invention.

[0014] Moreover, as the film surface component said to this invention and coupling agent which can react, the coupling agent of an acrylic silane system, an amino silane system, or an epoxy silane system is mentioned as the film surface component of a polyimide film, and coupling agent which can react, for example.

[0015] If it enumerates concretely, by the acrylic silane system, gamma-methacryloxypropyl trimethoxy silane, gamma-methacryloxypropyl triethoxysilane, gamma-methacryloxypropylmethyldimethoxysilane, gamma-methacryloxypropylmethyldiethoxysilane, gamma-acryloxypropyltrimethoxysilane, gamma-acryloxypropylmethyldimethoxysilane, etc. can be mentioned.

[0016] By the amino silane system, moreover, gamma-aminopropyl trimethoxysilane, gamma-aminopropyl triethoxysilane, gamma-aminopropyl methyl dimethoxysilane, gamma-aminopropyl methyldiethoxysilane, N-phenyl-gamma-aminopropyl trimethoxysilane, N-(phenylmethyl)-gamma-aminopropyl trimethoxysilane, N-methyl-gamma-aminopropyl trimethoxysilane, N and N, and N-TORIMECHIRU-gamma-aminopropyl trimethoxysilane, N, N, and N-tributyl-gamma-aminopropyl trimethoxysilane, N-beta (aminoethyl) gamma-aminopropyl trimethoxysilane, N-beta (aminoethyl) gamma-aminopropyl methyl dimethoxysilane, N-beta (aminoethyl) gamma-aminopropyl triethoxysilane, N-omega (amino hexyl) gamma-aminopropyl trimethoxysilane, N{N'-beta(aminoethyl)}-beta (aminoethyl) gamma-aminopropyl trimethoxysilane, etc. can be mentioned.

[0017] By the epoxy silane system, beta-(3, 4-epoxycyclohexyl) ethyl trimethoxysilane, gamma-glycidoxypropyltrimethoxysilane, gamma-glycidoxy propyltriethoxysilane, gamma-glycidoxypropylmethyldiethoxysilane, gamma-glycidoxy propyl methyldimethoxysilane, etc. can be mentioned.

[0018] When several sorts may be mixed and used and it performs surface treatment of a polyimide film even if it uses these coupling agent independently and, it is used suitably. In addition, the film surface component of the synthetic-resin film which can be applied to the above-mentioned this invention including synthetic-resin films other than a polyimide film, for example, polyester film, and a polyamide film can react, and these coupling agent can be used for the surface treatment of various synthetic-resin films.

[0019] Although rubbing is mechanically carried out with the solution of the above-mentioned coupling agent in the surface treatment method of this invention, as a solvent which melts coupling agent, it is independent, or water or an organic solvent is mixed and used. The following can be illustrated as an organic solvent here. Aromatic-hydrocarbon system solvents, such as ketone system solvents, such as alcoholic system solvents, such as SORUMIKUSSU which is a methanol, ethanol, propanol, isopropanols, or these mixed solvents, an acetone, MEK, 2-pentanone, and 3-pentanone, toluene, and a xylene, etc. are mentioned. Even if it uses independently, these may mix several sorts and may be used.

[0020] In addition, as for the concentration of the coupling agent in the solution of coupling agent, it is desirable that it is 0.01 % of the weight - 50 % of the weight, and it is desirable that it is 0.05 more % of the weight - 20 % of the weight. if the concentration of coupling agent is too high, unevenness will see

on a synthetic-resin film front face -- having -- an exterior -- it is because sufficient effect will no longer be discovered if it becomes less desirable and the concentration of coupling agent is too low conversely [0021] As mentioned above, although the example of the surface treatment method of the synthetic-resin film concerning this invention was explained, this invention is not limited only to these examples, and as shown in drawing 2, it is flooded with the solution 13 of coupling agent in a film 16, and the processor 26 constituted so that the roll 12 for rubbing might be formed in the both sides and a film 16 might be inserted may be made to perform surface treatment of film both sides simultaneously. Moreover, as a method of performing surface treatment of film both sides simultaneously, as shown in drawing 3, the position of the roll 12 for rubbing can be shifted and it may arrange, and the tension which starts a film 16 by this can be made small, and conveyance of a film can be made smooth. In addition, as a method of infiltrating a solution 13 into the roll 12 for rubbing, the roll 12 for rubbing is made to flood with a solution 13, and may not be infiltrated, from the upper part, a solution 13 is covered, and may be infiltrated into the roll 12 for rubbing, or a solution 13 may be drawn in the roll 12 for rubbing, and you may constitute so that a solution 13 may ooze from the inside.

[0022] Moreover, that the method of carrying out an air drying as the dryness method may be used, and it is not necessary to necessarily form a drying furnace 14 etc. can carry out this invention in the mode which added improvement which becomes various based on this contractor's knowledge within limits which do not deviate from the meaning, change, and correction.

[0023] Hereafter, although an example explains this invention concretely, this invention is not limited only to these examples.

[0024] Example Surface treatment of the polyimide film of 25-micrometer \*\* was carried out using the almost same processor as what was shown in 1 drawing 1. Drying temperature is 120 degrees C and line speed is 5 m/min. It carried out and the nonwoven fabric roll was used for the roll for rubbing. Coupling agent used gamma-methacryloxypropyl trimethoxy silane, and adjusted and used it for the 0.5wt% solution by using a methanol / water =50 / 50 (w/w) as a solvent.

[0025] The following examinations were performed in order to evaluate the adhesive property before and behind adhesive setting about a processing film.

[0026] After laminating the evaluation processing film of the adhesive property before hardening, and Du Pont piler RAKKUSU by the 185-degree C hot calender roll (3 kgf/cm pressure 2), it cut with a width-of-face [ of 1cm ] x length of 20cm in the shape of a strip of paper, the piler RAKKUSU side was turned down, and it fixed to the plate with the double-sided tape. And the processing film-piler RAKKUSU interface was torn off at 90 degrees of exfoliation angles, the load at that time was measured, and the value was made into the bond strength before hardening. The result is shown in Table 1.

[0027] After laminating a processing film and piler RAKKUSU like evaluation of the adhesive property before evaluation hardening of the adhesive property after hardening, by this hot calender roll, copper foil (1-oz electrolytic copper foil) was laminated, 185-degree C oven performed the hardening reaction for 1 hour, and FCCL (a film and copper foil plywood) was produced. About obtained FCCL, it is JIS. C According to 5016, it \*\*\*\*\*ed to 5mm width of face, and copper foil was exfoliated at 90 degrees, the Peel intensity was measured, and the value was made into the bond strength after hardening. The result is shown in Table 1.

[0028]

[Table 1]

	硬化前接着強度 (gf/cm)	硬化後接着強度 (kgf/cm)
実施例 1	2 5 0	2. 1
実施例 2	2 0 0	2. 2
実施例 3	8 0	2. 2
実施例 4	1 5 0	1. 8
比較例 1	5	0. 6
比較例 2	6	1. 3
比較例 3	6	1. 4

[0029] Example 2 coupling agent was changed into N-phenyl-gamma-aminopropyl trimethoxysilane, and surface treatment of a polyimide film was performed like the example 1. About the processing film, adhesive evaluation before and behind adhesive setting was hereafter performed like the example 1. The result is shown in Table 1.

[0030] Example 3 coupling agent was changed into N-beta (aminoethyl) gamma-aminopropyl trimethoxysilane, and surface treatment of a polyimide film was performed like the example 1. About the processing film, adhesive evaluation before and behind adhesive setting was hereafter performed like the example 1. The result is shown in Table 1.

[0031] Example 4 coupling agent was changed into gamma-glycidoxypopyltrimetoxysilane, and surface treatment of a polyimide film was performed like the example 1. About the processing film, adhesive evaluation before and behind adhesive setting was hereafter performed like the example 1. The result is shown in Table 1.

[0032] Example of comparison For 1 comparison, adhesive evaluation before and behind adhesive setting was hereafter performed on the polyimide film used in the examples 1-4 like the example 1, without performing surface treatment. The result is shown in Table 1.

[0033] Example of comparison It is power flux density to the polyimide film used in the examples 1-4 for 2 comparison. 230 w-min / m<sup>2</sup> The corona treatment was given on conditions and adhesive evaluation before and behind adhesive setting was hereafter performed like the example 1. The result is shown in Table 1.

[0034] Example of comparison They are a type of gas Ar and a pressure to the polyimide film used in the examples 1-4 for 3 comparison. 760 mmHg, power flux density 400 w-min / m<sup>2</sup> Plasma treatment was performed on conditions and adhesive evaluation before and behind adhesive setting was hereafter performed like the example 1. The result is shown in Table 1.

[0035]

[Effect of the Invention] According to the surface treatment method of the synthetic-resin film concerning this invention, rubbing of the front face of a synthetic-resin film is mechanically carried out with a film surface component and the solution of coupling agent which can react, by the easy art of making it dry after that, the brittle layer on the front face of a film can be removed, and chemical modification on the front face of a film can be performed simultaneously. Consequently, the adhesive property of a film is improved, and even if the state of adhesives is in which state of a hardening state, the state where it does not harden, and a semi-hardening state, the film in which a good adhesive property is shown can be obtained. That is, the surface treatment method of the synthetic-resin film concerning this invention offers the surface treatment [ which can solve the conventional problem ] method which was simple and was excellent.